

STUDIES ON OVERVOLTAGE

VI. The Mechanism of the Transfer of Electrolytic Hydrogen and Oxygen Through Thin Sheets of Platinum and Palladium.

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STUDIES ON OVERVOLTAGE.

VI. The Mechanism of the Transfer of Electrolytic Hydrogen and Oxygen Through Thin Sheets of Platinum and Palladium.¹

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ABSTRACT.

The nature of the diffusion of anode and cathode polarization products through thin sheets of platinum and palladium has been investigated and it was found that no diffusion of electromotively active material occurs through solid metal, even though very thin. When a change in the potential of the back of a thin electrode occurs, it is found that the metal is not perfectly continuous and that a small solution connection has been established in the discontinuities through which a small amount of current flows and charges the back. The previous work in this field is critically reviewed and it is found that the results of earlier workers confirm the present findings. Inconsistencies in the previous work are satisfactorily explained.

A general theory is developed to explain the results obtained in a number of different fields of investigation. A satisfactory theory of the blistering of metals is proposed. The value of the present research in the clarification of the theory of polarization and overvoltage is discussed.

INTRODUCTION.

It has been shown in the previous papers of this series⁴ that a "transfer resistance" component of overvoltage does not exist under the conditions studied. It was erroneously stated in one of the earlier articles⁵ that the concept of transfer resistance was introduced by

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⁴ Trans. Am. Electrochem. Soc., **45**, 311 (1924); **47**, 227 (1925); J. Phys. Chem., **36**, 1156, 1166, 2437 (1932).

⁵ Trans. Am. Electrochem. Soc., **47**, 227 (1925).

Gore in 1885. This impression was gained from the publications of Newbery,⁶ who makes the same error. The theory was originally sponsored mainly by Fechner,⁷ who attempted to apply Ohm's law to electrolytic conduction, and who considered all of the phenomena of polarization and overvoltage to be due to a transfer resistance. This view was immediately contested by Ohm, and a few years later by Lenz, while Poggendorff joined Fechner as a staunch defender of the concept. It was soon evident that the back electromotive force of polarization was responsible for a large part of the opposition to the flow of current, and ultimately Poggendorff abandoned the assumption of a transfer resistance completely.

A detailed review of these early controversies has been given by Ostwald⁸ who considers that Lenz succeeded in showing that there is ordinarily no transfer resistance. The non-existence of transfer resistance was also shown by Nernst and Haagn,⁹ whose work appears to have received but little attention in this connection. Baars¹⁰ made some rough measurements by the method of Nernst and Haagn to confirm his oscillographic results, and found that from current densities of 10^{-3} amp./cm.² upwards, no resistance changes greater than 0.5 ohm were to be observed. He concludes that overvoltage measurements by the direct method at current densities higher than 10^{-3} amp./cm.² are not incorrect, due to transfer resistance to an amount exceeding a few millivolts, that is, not to any noteworthy extent.

At the beginning of the present work the authors were not aware of the method of Nernst and Haagn, and sought to find a satisfactory direct method of measuring transfer resistance under the unusual conditions where such a quantity perhaps exists. Conversely it was desired to show that nothing of the nature of transfer resistance exists under the ordinary conditions of electrolysis.

The most generally accepted theories of polarization and overvoltage consider that the electrode potentials are due to the concentration of electromotively active hydrogen or oxygen dissolved in the surface of the metal of the electrode. The different potentials at different points on the surface of the same electrode corresponding to different current densities are considered to be due to a difference in the con-

⁶ Trans. Faraday Soc., **15**, 126 (1919); Trans. Am. Electrochem. Soc., **58**, 215 (1930).

⁷ "Massbestimmungen über die galvanische Kette," 260 p., Leipzig (1831).

⁸ "Elektrochemie—Ihre Geschichte und Lehre," Leipzig (1896) (See esp. p. 420-425, 645, 673-677, 903).

⁹ Z. Elektrochem., **2**, 493 (1896); **3**, 421, 470 (1897); Z. physik. Chem., **23**, 97 (1897).

¹⁰ Sitzungsber. Ges. Naturwiss. Marburg, **63**, 301 (1928).

centration of gas dissolved in the surface of the metal at the two points, a high concentration of gas corresponding to a high potential

Starting from this point of view, it was felt that if sufficiently thin platinum or palladium electrodes were used, the true polarization potential would be the same on both sides of the electrode if a current were passed into one side only, and any higher potential on the side into which the current was flowing would be due to a non-diffusible component of overvoltage such as a transfer resistance presumably would be. In this way the platinum or palladium foil would act as a semi-permeable membrane through which only polarization and overvoltage could pass.

The original hopes failed to be realized because it was found that, whatever it is that causes polarization and overvoltage, it is incapable of diffusing through platinum or palladium, and electrolysis on one side of a thin sheet of metal is not made evident by changes in potential on the opposite side. A change in potential of the back of an electrode only occurred if the metal was discontinuous and a slight solution connection between the front and back was made through pores.

The reason why previous workers failed to discover this fact was because they generally investigated only the change in potential with time of the back of an electrode when a fixed current density or potential was applied to the front. A systematic investigation of the variation of the potential of the back of the electrode with varying current density applied to the front, such as is reported here, points very strongly to the conclusion that the phenomena are due entirely to the porosity of the thin sheets of metal.

HISTORICAL.

The diffusion of electrolytic hydrogen and oxygen through thin sheets of platinum and palladium was first investigated by means of potential measurements by Crova,¹¹ Helmholtz and Root¹² and Beetz.¹³ Bellati and Lussana¹⁴ found that cathodic hydrogen readily diffused into the inside of a closed iron tube, and would build up to pressures as high as 20 atm. without approaching an end in the pressure increase.

¹¹ *Les Mondes*, **5**, 210 (1864); *Chem. News*, **11**, 74 (1865).

¹² *Monatsber. Ber. Akad.*, p. 217 (1876); *Chem. Centralblatt*, p. 401 (1876); *Phil. Mag.* (5), **2**, 153 (1876); *Ann. phys.*, **159**, 416 (1876); *Ges. Abhd.* **I**, 835 (1882).

¹³ *Sitzungsber. Bayer. Akad. Munich, Math.-phys. Klasse*, **8**, 140 (1878); *Wied. Ann.*, **5**, 1 (1878); *Phil. Mag.* (5), **7**, 1 (1879).

¹⁴ *Atti ist. Veneto* (6), **7**, 1321 (1889); (7) **1**, 1173 (1890); (7) **2**, 987 (1891). Abstracts: *Beiblätter*, **14**, 239 (1890); **15**, 333 (1891); **18**, 434 (1894).

Shields¹⁵ confirmed their work but found that hydrogen would not diffuse through lead, platinum, or palladium.

A pressure of 26 atm. was later attained on the inside of iron tubes by Charpy and Bonnerot,¹⁶ and pressures in the neighborhood of 300 atm. were secured by Bardenheuer and Thanheiser.¹⁷ Winkelmann¹⁸ showed that the rate of diffusion was almost proportional to the cathode current density, and that there was a direct proportionality between the rate of diffusion and the "effective potential," the latter being defined as the difference between the cell voltage with current flowing and the back electromotive force on open circuit. The diffusion through iron tubes was also studied by Fuller,¹⁹ Bodenstein,²⁰ Knobel and Norton,²¹ and Borelius and Lindblom.²²

Nernst and Lessing²³ showed by means of potential measurements on sheets of varying thickness that hydrogen diffused through palladium, but not through platinum, since thick sheets of the latter metal were completely impermeable. Lessing²⁴ later re-investigated the diffusion of hydrogen through palladium since Winkelmann's "effective potential" was different from the cathode potential of the Nernst theory. Wilke²⁵ and Drucker²⁶ were not entirely successful in the production of hydrogen electrodes using thin palladium tubes.

Schmidt and Lücke²⁷ claimed to have shown that Nernst and Lessing were wrong, and that true diffusion of hydrogen through platinum does take place. Köhler,²⁸ working in Nernst's laboratory, later found that true diffusion of hydrogen occurs through both platinum and palladium, in agreement with Schmidt and Lücke.

A relationship between the concentration and composition of the electrolyte, the charge on the hydrogen bubbles at the cathode, and the absorption of hydrogen was pointed out by Coehn²⁹ and Coehn

¹⁵ Chem. News, **65**, 195 (1892).

¹⁶ Compt. rend., **154**, 592 (1912); **156**, 394 (1913).

¹⁷ Mitt. Kaiser-Wilhelm Inst. Eisenforsch., **10**, 323 (1928); Stahl Eisen, **49**, 1185 (1929); Z. tech. Physik, **10**, 143 (1929).

¹⁸ Ann. Physik., **17**, 589 (1905); Festschrift A. Wüllner, p. 36 (1905).

¹⁹ Trans. Am. Electrochem. Soc., **36**, 113 (1919); Gen. Elec. Rev., **23**, 702 (1920).

²⁰ Z. Elektrochem., **28**, 517 (1922); Verhandl. deut. phys. Ges. (3), **3**, 40 (1922).

²¹ J. Math. Phys., **5**, 75 (1926).

²² Ann. Physik., **82**, 201 (1927).

²³ Nachr. kgl. Ges. Wiss. Göttingen (Math.-Phys. Klasse), p. 146 (1902).

²⁴ Verhandl. deut. physik. Ges., **8**, 569 (1906).

²⁵ Z. Elektrochem., **19**, 857 (1913).

²⁶ Z. Elektrochem., **33**, 504 (1927).

²⁷ Z. Physik., **8**, 152 (1922).

²⁸ Z. physik. Chem., **135**, 369 (1928).

²⁹ Z. Elektrochem., **29**, 306 (1923).

and Baumgarten.³⁰ Alekseev and Savinina³¹ investigated the diffusion of cathodic hydrogen through a number of metals which had not been studied previously, while Alekseev and Polukarov³² showed the effect of impurities such as mercury, arsenic or lead in the electrolyte in causing the absorption of hydrogen by iron and steel, with consequent embrittlement. More recently, Aten and Zieren³³ and Aten and Blokker³⁴ also investigated the effect of impurities in raising the cathode potential and accelerating the rate of diffusion, but were unable to find any acceptable relation between current strength, electromotive force, and diffusion velocity.

The diffusion of electrolytic polarization has been studied also by Schmidt and his students³⁵ in connection with the hydrogen theory of passivity.

A very rapid increase in the photoelectric effect on one side of thin metal sheets has been found when the opposite side was exposed to anode or cathode polarization. Eichler³⁶ found platinum, palladium and iron to behave the same in this respect and comments on the apparent contradiction to the results of Nernst and Lessing, who found that hydrogen diffused through palladium but not platinum. Ernst³⁷ and DümpeImann and Hein³⁸ also investigated this effect.

Arons³⁹ discovered that extremely thin diaphragms of gold, silver or platinum offer practically no resistance to the flow of current between anode and cathode at moderate current densities due to the inter-diffusion and neutralization of the anode and cathode polarization. A controversy was started which lasted a number of years⁴⁰ and appeared to end with the work of Nernst and Scott⁴¹ and Scott,⁴²

³⁰ Z. physik. Chem., **130**, 545 (1927); Baumgarten, Diss. Göttingen, 39 p. (1926).

³¹ J. Russ. Phys. Chem. Soc. (Phys. Part), **56**, 560 (1924).

³² Z. Elektrochem., **32**, 248 (1926); J. Russ. Phys. Chem. Soc. (Chem. Part), **58**, 511 (1926).

³³ Rec. trav. chim. P. B., **49**, 641 (1930).

³⁴ Rec. trav. chim. P. B., **50**, 943 (1931).

³⁵ E. Grave, Z. physik. Chem., **77**, 513 (1911); W. Rathert, Z. physik. Chem., **86**, 567 (1914); G. C. Schmidt, Trans. Faraday Soc., **9**, 257 (1914) and Chem. News, **109**, 38, 51 (1914); J. Stapenhorst, Z. physik. Chem., **92**, 238 (1917); G. C. Schmidt, Z. physik. Chem., **106**, 105 (1923).

³⁶ Z. wiss. Phot., **16**, 10, 60 (1916).

³⁷ Z. wiss. Phot., **17**, 35, 68 (1917).

³⁸ Z. Physik., **22**, 368 (1924).

³⁹ Wied. Ann., **46**, 168 (1892); Phil. Mag., **34**, 140 (1893).

⁴⁰ J. Daniel, Wied. Ann., **49**, 281 (1893); Phil. Mag., **37**, 185, 288 (1894); Phys. Rev., **1**, 241, 351 (1894). H. Luggin, Wied. Ann., **56**, 347 (1895). W. Löb and H. Kaufmann, Z. Elektrochem., **2**, 341 (1895). K. Ochs, Z. Elektrochem., **2**, 398 (1895). L. Arons, Wied. Ann., **57**, 201 (1895). H. Luggin, Wied. Ann., **57**, 700 (1896). L. Arons, Wied. Ann., **58**, 680 (1896). G. P. Grimaldi and G. Platania, Atti acca. Lincei (5), **5**, Part 2, 100 (1896); Il Nuovo Cim. (4), **4**, 149 (1896). W. Löb, Z. Elektrochem., **3**, 185 (1896). H. Kaufmann, Z. Elektrochem., **3**, 237 (1896). W. Nernst, Jahrb. der Elektrochemie, **3**, 33 (1897).

⁴¹ Wied. Ann. Jubelband, **63**, 386 (1897).

⁴² Ann. Physik., **67**, 388 (1899).

who showed that the current flowed through pores in the case of gold, and even with platinum there was no depolarization with sheets as thin as 0.001 mm. if the sheets were non-porous.

SUMMARY OF PREVIOUS WORK.

Previous workers appear to be unanimous in considering that electromotively active or other hydrogen may dissolve in and diffuse through a number of metals and appear on the opposite side of a thin sheet, either in the form of gaseous hydrogen or a more negative potential of the back. The only noteworthy exception was Nernst and Lessing,²³ who considered that no diffusion occurred with platinum except through pores in the metal; true diffusion taking place through palladium nevertheless. However, a recent paper emanating from the Nernst laboratory²⁸ reverts to the view that true diffusion also occurs through platinum.

The diffusion of oxygen or anode polarization has not been investigated to any great extent, but whenever such measurements have been made, diffusion was generally found to occur.

INCONSISTENCIES IN THE PREVIOUS WORK.

If hydrogen can diffuse through metals such as platinum and palladium, one would expect a certain amount of reproducibility and quantitative agreement in the results obtained. There does not seem to be any agreement between the solubility of hydrogen in metals and the rate of diffusion of cathodic hydrogen or cathode polarization. It is also noteworthy that anode polarization generally diffuses as well as cathode polarization.

In spite of the extremely high solubility of hydrogen in palladium, it has been found not to be as permeable to hydrogen as iron, and frequently it is found to be "passive" to the absorption of hydrogen and only takes up large amounts after "activation" by repeated absorption and desorption, or by making it anode in the case of electrolytic experiments.

Nickel was sometimes found to be extremely permeable to electrolytic hydrogen and sometimes did not show any appreciable permeability. Hydrogen gas is almost completely insoluble in platinum at room temperature and yet considerable diffusion of electrolytic hydrogen has been found. It is frequently assumed that atomic or "nascent" hydrogen is soluble in the metal under these conditions, but no very good direct proof of such solubility has been offered. Hydrogen is

much more soluble in copper at room temperature than in platinum, yet no diffusion of electrolytic hydrogen through copper has been found. The addition of nickel and chromium to iron made it impermeable in spite of the solubility of hydrogen in all three metals.

While most investigators from the time of Helmholtz to the present have considered that there was a direct relation between the concentration of gas dissolved in a metal and its potential, no such relation appeared to be evident from the work reviewed here, and there is considerable evidence for the lack of any such relation.

The fact that the rate of diffusion varies with the current density more than with the potential at which hydrogen is liberated is difficult to explain, and no explanation appears to have been attempted. Another curious fact was that hydrogen evolved from acids appeared to diffuse through iron about three times as fast as that from alkaline solutions.

EXPERIMENTAL.

A diagram of the apparatus used in this work is shown in Fig. 1 and a photograph of most of the set-up in Fig. 2. The electrodes

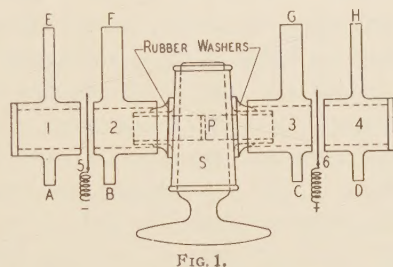


FIG. 1.

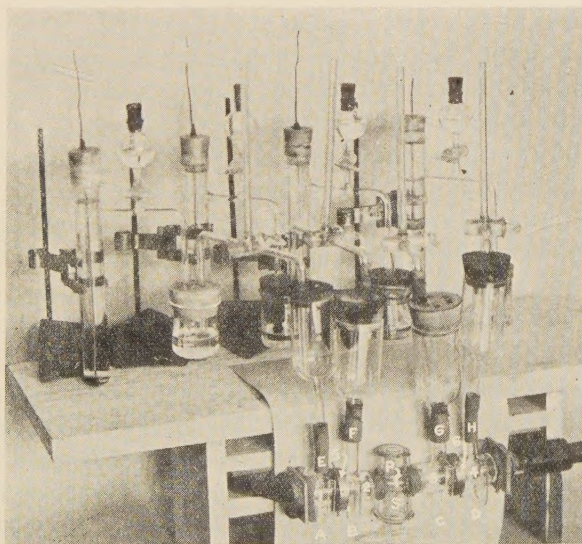


FIG. 2

and glass compartments were arranged as shown and then clamped together from the ends. Rubber gaskets were used on each side of the electrodes to protect the thin sheets of metal and make a solution-tight connection. The compartments in front of the anode and cathode were connected through a 10 mm. glass stopcock *S* which was fitted with a plug of filter paper *P* to reduce diffusion to a minimum.

After the apparatus was assembled it was filled with solution through the four inlet tubes, *A*, *B*, *C*, and *D*. These tubes also served for bubbling gas through the solution when it was desired to saturate the solution around the cathode with hydrogen and around the anode with oxygen. When the gases were used, they passed out through the outlets *E*, *F*, *G* and *H* and into carbon tubes, partly filled with solution and stoppered at the top, but with a small outlet to the atmosphere. Connecting syphons, made from two of the tubes of three-way glass stopcocks, passed through the stoppers and made connection to intermediate beakers containing the same solution as that in the cell and into which the tips of the four reference electrodes also dipped. The stopcocks were plugged with filter paper to minimize diffusion and the solution level was kept higher in the carbon tubes than in the intermediate beakers at all times so that diffusion was always away from the cell. This was necessary because the diffusion of small amounts of mercury from the $2N$ Hg_2SO_4 reference electrodes would markedly affect the electrode potentials.

Two normal H_2SO_4 was used as the electrolyte. The two center outlet tubes *F* and *G* were large so as to permit the insertion of exploring reference electrode tips to press directly against the surface of the anode and cathode. The platinum and palladium foil used was obtained from the American Platinum Works, Newark, N. J., and was stated to be C. P. (absolutely free from base metals) and delivered in the hard drawn state without annealing or recrystallization.

All measurements were made at room temperature, which was generally constant to within one to two degrees of 25°C . The compartments were numbered 1, 2, 3 and 4, as shown, and the reference electrode connected to each compartment was numbered correspondingly. The cathode and anode were numbered 5 and 6, respectively, or corresponding pairs of higher numbers. To determine the potentials of the back and front of the cathode and front and back of the anode, the electrode combinations 1-5, 2-5, 3-6 and 4-6 were measured. Frequently a number of other electrode combinations were studied but these were not important. The potentials have been plotted directly

as measured, with reference to the 2 *N* Hg₂SO₄ electrode. Current densities are given in mili. amp./cm.². The heavy-walled glass tubing used to make up the sections of the cell had an inside diameter of about 1.8 cm. and the anode and cathode areas were about 2.5 cm.².

An ordinary student's potentiometer was used since greater sensitivity was not necessary. The galvanometer was of the moving coil, mirror and scale type, with a resistance of 362 ohms and a sensitivity of 520 megohms. It was placed in series with a 10,000-ohm resistance.

The procedure generally used was to make any desired change in the current and applied potential, and then after waiting about 3 to 6 minutes, to measure the potentials as rapidly as possible. The applied potential remained approximately constant for each single set of readings, while the current decreased slowly in most cases, due to the increase in overvoltage with time.

Twelve preliminary experiments were carried out with a smaller apparatus having an electrode area of about 1.4 cm.². This cell had only a single center compartment between the cathode and anode. Saturated KCl was used throughout in conjunction with three saturated calomel electrodes. Two sheets of Pt 0.0015 in. (0.038 mm.) thick were used as cathode and anode. The anode was found to be very permeable to anode polarization, and the potential of the back followed that of the front rather closely. The cathode was not as permeable to hydrogen or cathode polarization, but the permeability increased somewhat during the experiments.

Irregularities were observed in the potential of the back of the cathode. At low current densities, the cathode generally seemed almost completely impermeable, but shortly after the decomposition potential had been exceeded the back of the cathode more or less suddenly became quite cathodic. Using the cathode as anode and vice versa, showed that the cathode behaved the same to anode polarization, while the anode was very permeable to cathode polarization. The permeability or lack of it appeared to be characteristic of each electrode. Platinizing the electrodes appeared to make them less permeable, particularly the cathode. These experiments merely served to indicate an irregularity in the diffusion through platinum, and were not understood at the time they were performed. Several experiments with silver electrodes 0.009 in. (0.229 mm.) thick showed them to be completely impervious to both anode and cathode polarization, and the potentials of the backs of the electrodes remained constant, regardless of the potential applied to the front.

In the next series of experiments, using the 4-compartment cell shown in Fig. 1 and 2, Pt foil 0.0005 in. (0.0127 mm.) thick was used and the electrodes were called No. 5 and No. 6. The 1 in. (25.4 mm.) square pieces of Pt foil were supported carefully by means of a ring of copper wire soldered to the four corners, and this wire also served to make electrical connection to the foil. The surprising result was obtained that this thinner Pt foil was at first less permeable to electrolytic hydrogen and oxygen than the sheets three times thicker which were used in the preliminary experiments. This was especially surprising at the anode, which remained completely impervious through-

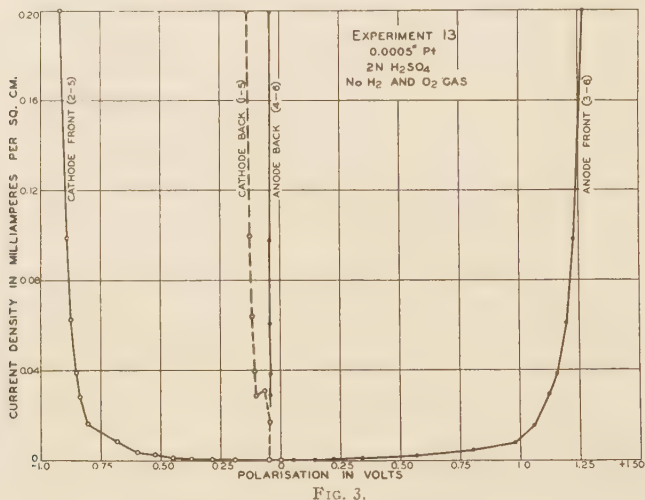


FIG. 3.

out experiments 13 to 18, inclusive. It was thought that perhaps the platinum might be permeable to chlorine, and in experiments 16 and 17 the effect of adding KCl to the 2N H₂SO₄ was determined, but no effect was noted. In experiment 18 the effect of using saturated KCl again and high current densities up to 60 mili. amp./cm.² was investigated, but electrode 6 appeared to be completely impervious to anode polarization, whether due to oxygen or chlorine.

The cathode (electrode 5) was also quite impervious to electrolytic hydrogen at first, as is evident from the results of experiment 13 shown in Fig. 3. A period of about three hours was occupied in reaching a current density of about 0.02 mili. amp./cm.² and during this time there was no noteworthy change in the potential of the back of the cathode. On increasing the current density further to about 0.03 mili. amp./cm.², the back of the cathode did become slightly more

negative and this change was followed for about 15 minutes until it had practically stopped. Additional increases in current density caused only a small additional increase in the potential of the back of the cathode.

In experiment 14 and a number of the succeeding experiments, hydrogen and oxygen gas were bubbled around the cathode and anode respectively during polarization. The oxygen had no effect. The hydrogen caused the cathode to take on a somewhat more negative potential at the beginning of the experiments, and merely precluded the possibility of making measurements at the lowest current densities and less



FIG. 4.

negative potentials. Sometimes, especially if the electrode in question had previously been used as anode, the hydrogen gas caused the cathode to take on a potential approaching that of a true hydrogen electrode in 2N H₂SO₄ (−0.670 v. referred to the 2N Hg₂SO₄ electrode), but generally the potential was about 0.3 v. less negative.

The results of experiment 14 are shown in Fig. 4. The potentials of the front and back of the cathode are given with both increasing and decreasing current. The cathode was more permeable than before and the potential of the back sometimes jumped up to higher values, and having attained them, sometimes fell back to lower values.

It was thought that the diffusion of potential to the back and its irregularity were perhaps due to traces of sodium or other alkali metals in the 2N H₂SO₄, and that the addition of a sufficient quantity of

an alkali metal salt to the solution would give a steady and higher potential on the back of the cathode due to the deposition and diffusion of small amounts of alkali metal. Additions of potassium salts were made in experiments 15, 16 and 17, and while the cathode continually seemed to show a potential on the back, no effect which could be definitely attributed to the addition was noted. The same type of irregularities was noted in experiment 15 with the $2N$ H_2SO_4 made $0.1N$ in K_2SO_4 as in experiment 14 without the addition. In experiment 16 they had diminished and in experiment 17, the results of which are shown in Fig. 5, the cathode was distinctly permeable and

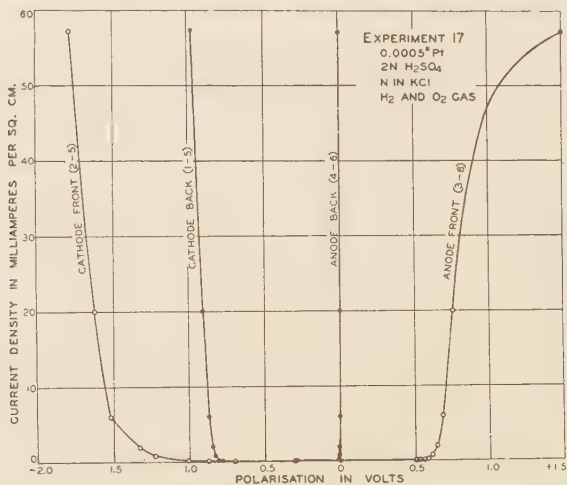


FIG. 5.

gave a more or less steady potential on the back. The potential of the front of the anode was low at low current densities in experiment 17 due to the depolarizing action of the KCl in strongly acid solution.

After experiment 18 the apparatus was taken apart, cleaned thoroughly and re-assembled. The results of experiment 19 are given in Fig. 6 and it is to be noted that the anode was now permeable to anode polarization. At the conclusion of experiment 19 the continuous evolution of hydrogen from a number of points all over the back of the cathode (electrode 5) was observed at the highest current density used. It occurred to the authors that with visible hydrogen evolution of this extent on the back of the cathode it should be an easy matter to obtain positive proof of the nature of the diffusion. By placing distilled water in compartment 1 and following any variation

in its pH with an indicator, a sensitive test for the nature of the phenomena should be obtained. If atomic or molecular hydrogen were diffusing through the metal according to the generally accepted theory, there would be no change in pH. One might consider from the work of Bowden⁴³ that perhaps the potential on the back of the cathode was due to the diffusion of traces of electronegative metals such as Na or K through the platinum, and that these would turn the distilled water alkaline on decomposing it.

Much to our surprise the test showed that the water in the chamber back of the electrode rapidly became acid, and that a stream of strongly

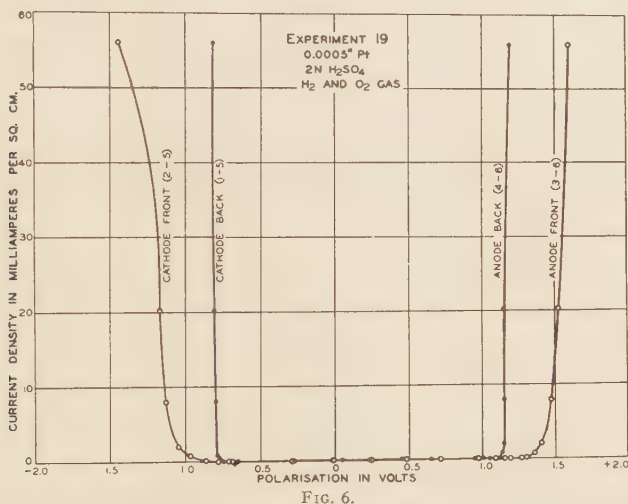


FIG. 6.

acid solution flowed down the back of the electrode. It was at once evident that both of the above theories were incorrect and that there were actual pores in the metal through which the H₂SO₄ was flowing under a hydrostatic head of about 5 in. (12.7 cm.). The phenomenon was checked by adding some NaHCO₃ to the distilled water, which gave a continuous stream of CO₂ bubbles from the same points where hydrogen was evolved during electrolysis. A repetition of these tests in compartment 4 gave similar results and there appeared to be no doubt that the phenomena observed in all of the previous experiments were due to the porosity or non-porosity of the thin Pt electrodes. The potential of the front of an electrode diffused through to the back only if minute pores in the metal existed through which a slight solution connection to the back was established.

⁴³ Trans. Faraday Soc., 23, 571 (1927).

A more or less quantitative measure of the porosity of the electrodes was obtained by titrating the amount of H_2SO_4 which diffused through an electrode in 24 hours. It was found that about 0.1 cc. of 2*N* H_2SO_4 diffused through electrode 5 in 24 hours and about 0.01 cc. through electrode 6.

A calculation of the size of the pores in electrode 5 from the rate of flow gave a diameter of about 0.0001 in. (0.0025 mm.) assuming a single large cylindrical pore straight through the metal; assuming 10 pores gave a diameter of about 0.00006 in. (0.00152 mm.).

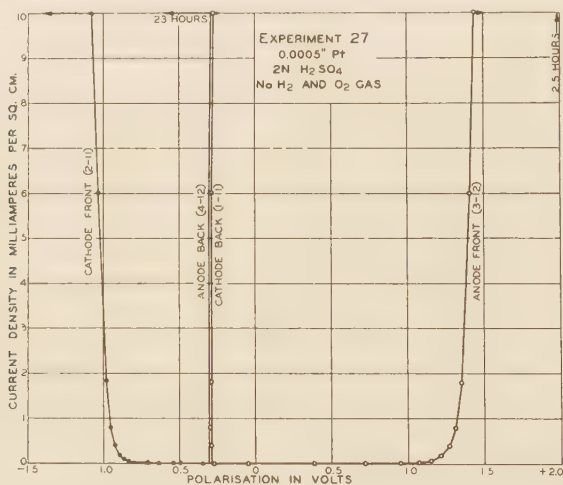


FIG. 7.

In experiments 20 to 25, inclusive, the effect of reversing the polarity was studied and it was found the same as in the preliminary experiments that the extent to which either cathode or anode polarization diffused through an electrode was a characteristic of that electrode and was a rough measure of its porosity. The effect of placing distilled water in compartments 1 and 4 at a 2 in. (5.1 cm.) higher level than the 2*N* H_2SO_4 in compartments 2 and 3 was also tried in order to fill the pores with water or at least a more dilute solution, and it was found that this usually reduced the potential of the back of the electrode considerably, as was expected. With solution of lower conductivity in the pores of the metal, less current could get through to charge the back of the electrode.

The experiments last mentioned above were not all strictly comparable because the porosity of the electrodes increased from one

experiment to the next, due either to the rather high current density used part of the time, or to the pressing of the exploring reference electrode tips against the front of the electrode. At the end of experiment 25 a porosity test showed that 0.40 cc. of $2N$ H_2SO_4 diffused through electrode 5 in 24 hours and 0.17 cc. through electrode 6.

In order to eliminate all deformation and strain of the electrodes in further experiments and make it possible to use even thinner foil, it was decided not to use the exploring reference electrode tips and

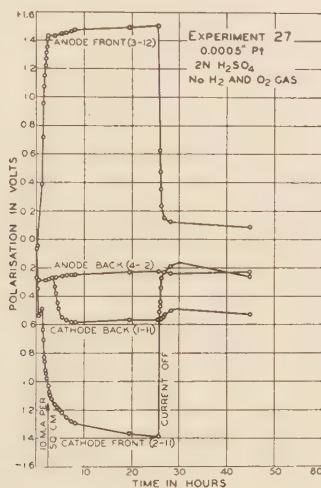


FIG. 8.

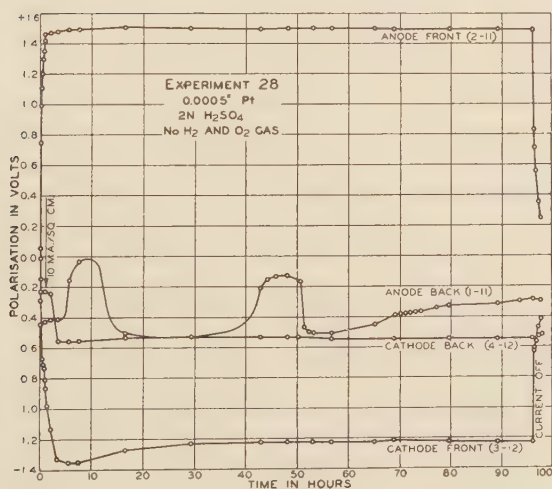


FIG. 9.

to construct holders for the foil such that it would be subjected to a minimum of handling. Eliminating the exploring electrode tips meant that a small IR drop would be included in the measured potentials of the front of the electrodes. This was not important at low current densities and was calculated to amount to about 0.025 mv. at 10 milliamp./cm.². At higher current densities it would, of course, increase and become relatively more important. It was not necessary to know the exact potential of the front of the electrodes in this work, however.

The authors concluded from these experiments that Pt foil of any thinness would be impenetrable to electrolytic polarization if it had

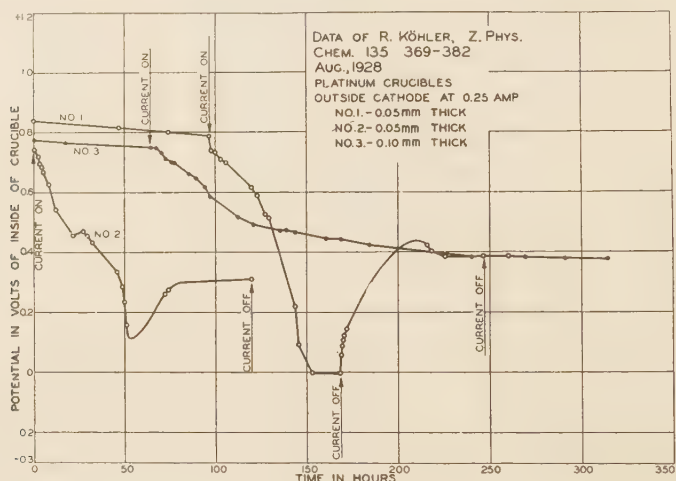


FIG. 10.

no mechanical defects and could be handled carefully enough. Since Pt and Pd foil 0.0001 in. (0.0025 mm.) thick was available, the brass electrode holders shown at 5 and 6 in Fig. 2 were constructed so as to be able to mount this foil in the apparatus without damaging it.

While the Pt and Pd foil 0.0001 in. (0.0025 mm.) thick appeared impervious to the naked eye, it was soon found that upon holding it up to a strong light a number of fine pores could be seen through which the light penetrated. This was true of every sample available. A few pores could also be seen in this way in electrodes 5 and 6, but none could be detected in unused Pt and Pd foil 0.0005 in. (0.0127 mm.) thick.

Experiment 26 was run with electrodes of 0.0001 in. (0.0025 mm.) Pt merely for purposes of comparison and it was found that the

curves were very similar to many obtained in previous experiments where the electrodes were porous.

Electrodes 11 and 12 of 0.0005 in. (0.0127 mm.) Pt were carefully mounted in the apparatus for experiments 27 to 32, inclusive. *N* KCl containing a few drops of methyl orange was placed behind the electrodes in compartments 1 and 4 in order to provide a quick test for porosity if it should suddenly develop. The attempt was made to cause these electrodes to become gradually more and more porous by using continually higher current densities up to about 240 mili. amp./cm.², but without success. The originally very slightly porous elec-

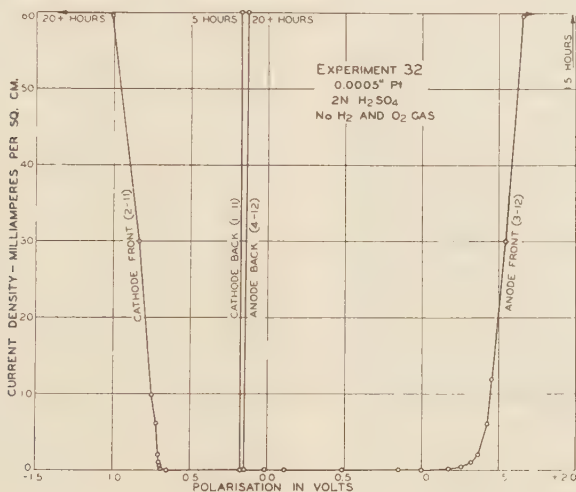


FIG. 11.

trodes became less porous during the experiments and in experiment 32 showed no signs of penetration at all. No tendency of the methyl orange behind the electrodes to turn red was observed, but it is possible that small amounts of acid diffused through which were insufficient to make a visible change.

The results of experiment 27 are shown in Fig. 7 and at first there was no evidence of penetration. After a few hours the potential of the back of the cathode began to change rather rapidly and in about an additional two hours had become about 0.3 v. more negative. The results plotted with respect to time are shown in Fig. 8. Fig. 9 shows the results of experiment 28 plotted with respect to time also. In experiment 28 the polarity was reversed and the back of electrode 12 became about 0.3 v. more negative and remained constant just as did

the back of electrode 11 in experiment 27. The back of electrode 11 showed some of the effects of anode polarization at first but then became cathodic again. This phenomenon was repeated somewhat later and then the potential finally became constant at an intermediate value.

A similar reversal of polarity at constant current density has been observed by Köhler²⁸ on the back of a cathode (crucible No. 2) and his results are shown in Fig. 10.

In experiment 31, current densities of over 240 mili.amp./cm.²

were used and maintained for a number of hours, but caused the backs of the electrodes to change only to an extent of about 0.2 v. This was about as high a current density as the apparatus could stand and heated the solution to about 60° or 65° C. while half as high a current density had only a slight heating effect.

The results of experiment 32 are shown in Fig. 11. The current density was raised to 60 mili.amp./cm.² in this case, which was 6 times as high as in experiment 27.

After 5 hours at this current the

potential of the back of the cathode was still constant and there was no sign of penetration. Hydrogen gas was now bubbled against the back of the cathode and immediately made it about 0.4 v. more negative or -0.580 v., but had no further effect. The potential of the hydrogen electrode in *N* KCl, referred to the 2 *N* Hg₂SO₄ electrode, was found to be about -1.032 v. The back of the anode showed no noteworthy variation during the entire period of the experiment, over 20 hours.

The electrodes were now taken out of the apparatus and examined. The general appearance of the front of the cathode (electrode 11) is shown in Fig. 12 at two magnifications. It was found to be covered with an adherent, dark brownish black deposit which was especially heavy at the bottom and in streaks extending upward from the bottom. The deposit was insoluble in conc. HNO₃ and was evidently Pt. The



FIG. 12. Appearance of Pt electrode 11.

solution and redeposition of Pt appeared to be a possible explanation of the decreasing porosity which was observed. A corresponding explanation at the anode seemed more difficult but it appeared that perhaps the formation of oxide had a tendency to stop up the pores.

The light spot at the top of Fig. 12 was due to a reflection from the bright metal surface. The rough appearance of the area subjected to electrolysis was found under the microscope to be due to a large number of small blisters which are shown in Fig. 13. A few blisters



FIG. 13. Front of electrode 11. $\times 160$

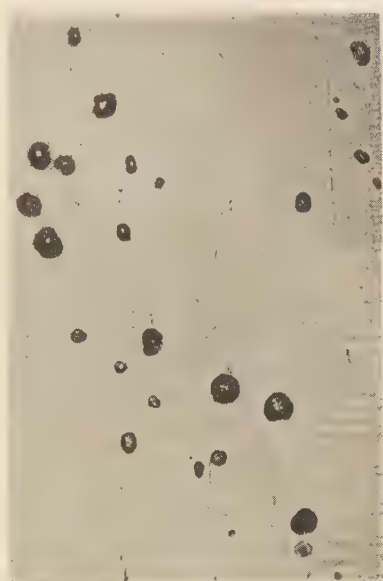


FIG. 14. Back of electrode 11. $\times 100$

also appeared on the back of the electrode, and Fig. 14 shows the appearance of a corresponding area on the opposite side to that shown in Fig. 13. None of the blisters was observed to have broken open, and the observations of other workers on the formation of "craters" in the surface of platinum cathodes probably relate to the use of still higher current densities.

Similar blistering of metals exposed to the action of cathodic hydrogen has been observed previously, and similar phenomena are quite common in the pickling of iron and steel.¹⁷ An explanation has been attempted recently by Hayes⁴⁴ who considers that the surface tension

⁴⁴ Trans. Am. Soc. Steel Treating, **17**, 527 (1930).

appeared that it would be necessary to deposit a dense, strong and soft layer of platinum in order to decrease the potential of the back below the decomposition potential. Since, so far as the authors are aware, the conditions for obtaining such a deposit have not been satisfactorily worked out, the experiments along this line were discontinued.

The apparatus was set up with electrodes 13 and 14 of Pd 0.0005 in. (0.0127 mm.) thick and with *N* KCl containing methyl orange in compartments 1 and 4. Very low current densities were used with Pd to avoid straining and damaging the electrode. The results of experiment 36 are shown in Fig. 15. The procedure used was to increase the current density and maintain it approximately constant, and then follow the variation of the potentials of the back of the electrodes until they became relatively constant.

The back of the cathode was very sensitive at first, and after the second and third increases in current actually showed a greater increase in potential on the back than on the front. The experiment was carried only to current densities slightly beyond the decomposition potential, but after exceeding about this value the cathode seemed to have become rather insensitive and impermeable. The potential of the back was relatively constant, even for many hours after opening the circuit. After 111 hours the attempt was made to depolarize the back of the cathode by bubbling through oxygen for 20 minutes, but only a small decrease of less than 0.050 v. resulted.

The back of the anode was rather insensitive at first but showed considerable response at the highest current densities. At the end of 24 hours a slight diffusion of acid through the anode was noted and it seemed as if there was also a very slight reddening of the methyl orange behind the cathode. The solution was withdrawn from compartments 1 and 4 and tested for sulfate with BaCl_2 . The solution from compartment 4 contained sulfate and a definite test for a slight trace was also obtained with the solution from compartment 1

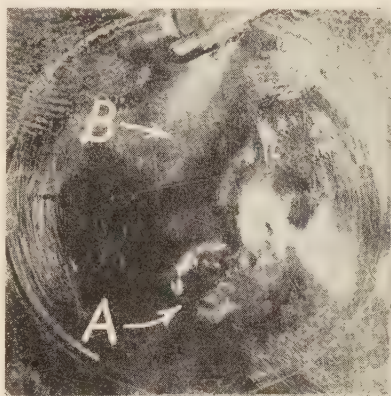


FIG. 16. Appearance of Pd electrode 13. x 2

which was not given by the original N KCl. No further visible change was observed in compartments 1 and 4 and the tests were not repeated. A more sensitive test for porosity seemed to be needed. At the conclusion of experiment 36 a porosity test was conducted with a 5 in. (12.7 cm.) head of a solution of 100 g. of eosin in a liter of 0.5 N NaOH, but there was no indication of diffusion after 4 days.

While the back of the cathode showed very little change on opening the circuit, the potential of the back of the anode fell rapidly.



FIG. 17. Electrode 13 at top. $\times 100$



FIG. 18. Electrode 13 on bump. $\times 100$

The electrodes were taken from the apparatus and examined. The general appearance of the front of the cathode is shown in Fig. 16. The total amount of current passed in experiment 36 was about 15 or 20 per cent of that required to saturate the cathode with hydrogen. An elliptical area at the bottom of the cathode, shown at *A* in Fig 16, was swelled up and expanded in the form of a bump, and all of the hydrogen appeared to have been absorbed over this area, because the rest of the surface was apparently unchanged. The light spot at the right-hand end of the bump is again a strong light reflection and does not indicate any surface irregularity.

It was found that while the main surface of the cathode was unaffected, the surface of the bump appeared under the microscope to be traversed by a number of lines of some sort. These same lines were in evidence on the back side of the bump also. The appearance of a point on the general surface of the cathode as at *B* is shown in Fig. 17 and that of the front of the bump in Fig. 18. The authors feel that these markings on the bump are either ordinary strain or slip lines, or they may be due to the formation of a new phase as a hydride of Pd. Tammann and his students⁴⁶ attribute surface irregularities on Pd which has absorbed hydrogen to a different expansion of the Pd along different crystallographic axes, so that some crystals project out of the surface farther than others.

DISCUSSION.

As the authors have already stated, they believe these experiments point very strongly to the conclusion that electromotively active hydrogen and oxygen do not diffuse through solid metals. Some of the principal phases of the experimental results which show this are:

1. The complete analogy between the diffusion of cathode and anode polarization. No essential difference was found during the investigation, yet if the diffusion were dependent upon solubility in the metal, pronounced differences would be expected in the permeability of Pt to cathode and anode polarization. The same should be true for Pd and there should also be a greater difference between Pt and Pd than was found.

2. The complete imperviousness sometimes attained to both cathode and anode polarization, especially with careful handling of the electrodes to avoid mechanical injury. Such imperviousness could not exist if diffusion through the solid metal were possible.

3. The sudden large increases frequently observed in the potential of the back of the electrode. If there were diffusion through the metal itself, a slow, steady change of a reproducible character would be expected.

4. The rapid depolarization of the back of the electrode which frequently occurs. If the entire body of metal were charged with electromotively active material, a much less rapid drop would be expected.

⁴⁶ Z. anorg. allgem. Chem., **172**, 43 (1928); **186**, 337 (1930); **188**, 396 (1930).

5. The intimate connection sometimes observed between the potential of the back and that of the front. Frequently an increase or decrease in the potential of the front is accompanied by an immediate increase or decrease in the potential of the back.

Of course it might be argued that the reverse of many of the above phenomena was sometimes observed, particularly in border line cases where it was often difficult or impossible to show the existence of porosity by independent means. To argue that some diffusion through the metal as well as through pores occurs in such cases, would seem to the authors to be without object. The phenomena have been shown to be largely due to porosity, and lacking any proof to the contrary, it would appear most logical to consider all of the changes observed to be due to porosity.

Even in experiments 27 to 32 with 0.0005 in. (0.0127 mm.) Pt, where no independent test for porosity was obtained, there were two very strong indications that the small diffusion was due to porosity. One was the erratic fluctuation of the potential of the back of the anode in experiment 28, which would be inexplicable without porosity considerations. The other was the complete imperviousness found in experiment 32.

The behavior of Pd was not investigated in as great detail as that of Pt, but similarities in the curves vouch for the identity of the nature of the phenomena. The absorption of hydrogen by palladium has been studied extensively. It is well established that the volume and electrical resistance increase and the tensile strength decreases when the metal absorbs hydrogen. Feussner⁴⁷ found that the hardness more than doubled. The authors feel that these extensive mechanical alterations probably affect the porosity.

Smekal⁴⁸ and others have shown that the surfaces of solids, even of single crystals, are not continuous but are covered with "Smekal cracks" which divide the surface into blocks of atoms roughly about 100 atoms on a side. It appeared to the authors that in the case of Pd perhaps hydrogen is adsorbed so strongly, and perhaps also has lateral mobility,⁴⁹ that it penetrates to the bottom of the Smekal cracks and there exerts sufficient force to extend the cracks and provide new surface and permit the adsorption of gas throughout the body of the metal.

⁴⁷ Metallwirtschaft, **11**, 450 (1932).

⁴⁸ J. W. McBain, "The Sorption of Gases and Vapours by Solids," p. 329, 356, and 507 (1932).

⁴⁹ See footnote 48, p. 352.

Views of this nature are by no means new and have previously been advanced in connection with the sorption of hydrogen by Pd.⁵⁰ A similar viewpoint would appear to the authors to be important in the diffusion of gases through metals at elevated temperatures, and the irregularities observed in the diffusion of hydrogen through Pd by Lombard and Eichner⁵¹ and through Fe by Jacquerod and Gagnebin,⁵² for example, are easily explained in this way.

Consistent with this view also are the measurements of Wien⁵³ who found that the polarization capacity of Pd increased about fourfold on charging it electrolytically with hydrogen and about 23 times on heating in a Bunsen burner, indicating corresponding changes in surface area. It might also be mentioned that Daniel⁴⁰ found that the maximum current which could flow through a palladium diaphragm without causing excessive polarization increased about four times with continued electrolysis, indicating probably a corresponding increase in porosity.

If this is the case, and the absorption of hydrogen does cause the formation of a network of extremely minute cracks through the Pd, the behavior is easily understood. The increase in volume and in electrical resistance, and decrease in tensile strength follow as a matter of course. The recently debated⁵⁴ effects of anode and cathode polarization in decreasing and increasing the resistance of Pd might be due to contraction or expansion of the metal, causing the units comprising it to make better or worse contact with each other.

With reference to the present work, it seems a satisfactory explanation of the phenomena to assume that the first absorption of hydrogen by Pd is accompanied by the production of minute openings through which small amounts of solution may diffuse and carry some current or polarization to the back. After the metal has expanded as much as possible, it is not unlikely that a certain amount of readjustment may occur and the sheet become less porous. This would account for the lack of permeability of used Pd, and the necessity for using fresh sheets in each experiment to get more or less reproducible results.

Thoma⁵⁵ found that some cathode polarization diffused along sheets of Pd a distance of 4 or 5 mm. from the part immersed in the elec-

⁵⁰ Trans. Faraday Soc., **14**, 232 (1919); **28**, 275, 408 (1932).

⁵¹ Bull. soc. chim., **51**, 1462 (1932).

⁵² Helv. Phys. Acta, **2**, 156 (1929).

⁵³ Ann. Physik., **8**, 372 (1902).

⁵⁴ Z. Physik., **69**, 253 (1931); **71**, 179 (1931); **78**, 815, 824 (1932).

⁵⁵ Z. physik. Chem., **3**, 69 (1889).

trolyte. Coehn and his students⁵⁶ have continued the investigation of the phenomenon and consider that it is due to the diffusion of protons, since the electromotively active material migrated toward the negative end of the circuit under the influence of an electric field. Franzini⁵⁷ has also followed a similar migration of hydrogen in an electric field along Ni and Fe wires by means of resistance changes.

A possible explanation is that small amounts of cathodically charged solution may creep through capillaries in the metal and carry some polarization a short distance. It also seems possible that this polarized solution may be capable of being caused to migrate further under the influence of an applied electrical field.

The results of the present investigation are helpful in the interpretation of the phenomena during the pickling of iron in acids, as has already been pointed out in connection with the explanation of the production of blisters. Polansky⁵⁸ gives an extensive bibliography of the effect of pickling on the properties of iron and steel. Mahin⁵⁹ found that the hydrogen in pickling does not appear to diffuse through the iron itself, but through visible discontinuities in the metal or near non-metallic inclusions. Several other more recent papers are of interest in this connection.⁶⁰ Extremely rapid diffusion of hydrogen sometimes occurs along the grain boundaries, resulting in embrittlement and weakening of the iron. It seems probable to the authors that the grain boundaries constitute an even greater discontinuity than Smekal cracks, and that there may be considerable spaces between the atoms of one crystal and those of the other through which ions and discharged hydrogen may pass.

Hevesy and Obrutsheva⁶¹ found that radioactive lead would not diffuse through a single crystal lead foil but the rate of diffusion through polycrystalline foil increased with the number of crystals and it seemed that diffusion only occurred over the surface and through grain boundaries.

Perhaps the most important result of the present work is to clarify the situation somewhat as regards the theory of polarization and over-voltage. The electromotive force is often considered to have its seat

⁵⁶ *Naturwissenschaften*, **16**, 183 (1928); *Z. Elektrochem.*, **35**, 676 (1929); *Z. Physik.*, **62**, 1 (1930); **71**, 179 (1931).

⁵⁷ *S. A. Rend. Lomb.*, (2) **64**, 1 (1931) [through *Physik. Ber.*, **12**, 2575 (1931)].

⁵⁸ Imhoff, "Pickling of Iron and Steel," p. 147 (1929).

⁵⁹ *Proc. Indiana Acad. Sci.*, **37**, 272 (1927).

⁶⁰ *Proc. Roy. Soc. (Lond.)*, **A123**, 171 (1929); *J. Iron Steel Inst.*, **119**, 179 (1929); *Mitt. Kaiser Wilhelm Inst. Eisenforsch.*, **14**, 229 (1932); *Z. Elektrochem.*, **39**, 252 (1933).

⁶¹ *Nature*, **115**, 674 (1925).

in the concentration of electromotively active gas dissolved in the metal. If the seat of the potential were within the metal, it would cause a very large current to flow in the opposite direction to the actual flow, which generally only causes a relatively small IR drop through the metal. Since metals possess metallic conductivity, a difference of potential cannot be maintained between two points in the metal except by a corresponding flow of current.

Differences in polarization or overvoltage amounting to over a volt may sometimes exist at two points on the surface of an electrode not far removed from each other, and it is impossible to consider them as being due to anything inside of the metal. It is obvious that the actual seat of the electromotive force is on the solution side of the interface. It would appear best to consider that the electrode charges the surface of the adjacent solution to an extent varying with the amount of current flowing into or out of the solution at that point.

This is consistent with the view of MacInnes and Adler⁶² that hydrogen overvoltage is due to a layer of solution next to the electrode which is supersaturated with molecular hydrogen. Tammann⁶³ and Kobosew and Nekrassow⁶⁴ found that a reducing substance was formed at the cathode in the electrolysis of pure NaOH and H₂SO₄ solutions which could be detected at a distance from the electrode. Such a material is probably closely connected with the cause of polarization and overvoltage.

ACKNOWLEDGMENT.

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DISCUSSION.

GUSTAF SODERBERG⁶⁵: During the last few years we have seen a very rapid development of new alloys, both ferrous and non-ferrous, several of which are being plated. The literature does not show a parallel development of pickling methods. The authors' contribution to the question of embrittlement is very welcome and I hope that further work will be done along the lines indicated and with particular reference to the composition, heat treatment and mechanical treatment of the steel.

A. H. W. ATEN⁶⁶ (*Communicated*): In our investigation on the diffusion of cathodic hydrogen through iron⁶⁷ we made some experiments on the diffusion

⁶² J. Am. Chem. Soc., **41**, 194 (1919).

⁶³ Z. anorg. allgem. Chem., **126**, 176 (1923).

⁶⁴ Z. Elektrochem., **36**, 529 (1930).

⁶⁵ Udylite Process Company, Detroit, Mich.

⁶⁶ Prof. of Electrochemistry, University of Amsterdam, Holland.

⁶⁷ Rec. **49**, 641 (1930); **50**, 943 (1931).

through palladium, and measured the potential at the back of a palladium sheet which was cemented between two obliquely ground glass tubes, the apparatus thus forming a V. The front of this palladium sheet was made cathode in a solution of sulfuric acid or of caustic soda. The back was in contact with a solution of the same composition. We found that, though hydrogen diffused through the palladium, the back of the metal never showed a potential as negative as the hydrogen—equilibrium potential. Probably this is due to the fact that the back surface of the metal is never saturated with hydrogen, the hydrogen diffusing faster from the surface into the liquid than it does through the metal to the surface. Only when the liquid at the back of the sheet was saturated with gaseous hydrogen from a hydrogen generator did this side of the metal show the true hydrogen potential, especially when it was covered with palladium black. But in this case it would give the hydrogen potential even without cathodic polarization of the front side.

We believe that, if the liquid at the back were completely shut off from the atmosphere, it should in the long run become saturated with hydrogen diffusing through the palladium, and so give the hydrogen potential. We do not think, however, that there is a special, active form of hydrogen diffusing through the metal, which could give rise to a potential more negative than the equilibrium potential.

A. L. FERGUSON: Assume that we have a long tube containing sulfuric acid with platinum foil electrodes completely filling the ends, and let one be the anode and the other the cathode; we might concentrate our attention on the cathode. After current had passed through such an outfit for several hours at a much higher current density than you would use in any plating, it was observed that the bottom part of the cathode was distinctly darker. This is shown in the photograph on p. 238. The darkening we showed to be platinum black. There are different points of view in regard to the cause for this darkening, but all would agree that the extent depends upon the current density and time. The darkening decreased in a fan shape from the very bottom to the top where there was none. The point I want to bring out is that, even in such a tube of uniform cross section from one electrode to the other, containing a solution of uniform concentration, the current density was much greater at the bottom than anywhere else, and decreased rather uniformly in all directions. We did not expect such an unequal distribution of current in an outfit of that kind. I have no explanation to offer for it.

